Room Temperature Mg Reduction of TiO₂: Formation Mechanism

and Application in Photocatalysis

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Experimental Section

1. Preparation of defective metal oxides

Metal oxide-Mg preparation: The metal oxide nanoparticles were pressed into cylinders (2 cm × 2 cm × 0.2 cm) using cold press machine (ASONE, TB-100H-V09). Pure magnesium sheets with thickness of 1 mm were cut into squares (10 cm × 10 cm) and then 500 ul HCl (0.5 mol L⁻¹) was dropped on each magnesium sheet. The cylinders were carefully placed between magnesium sheets to form sandwich structures, which subsequently were pressed by the cold press machine at 10 KN for 20 min. Afterwards, the metal oxides were taken out and washed several times with 0.5 mol HCl solution, deionized water and ethanol to remove remaining impurities. An ultrasonic machine was used for 1 h to uniformly disperse the samples followed by drying for further characterization.

Metal oxide-Li preparation: The metal oxide nanoparticles were pressed into cylinders (1cm \times 1cm \times 0.2cm) using cold press machine (ASONE, TB-100H-V09). 50 ul LiPF₆ was dropped on each lithium sheet (15.6 mm \times 0.25 mm). The remaining steps are the same as metal oxide-Mg.

Metal oxide-Al preparation: The experimental steps are the same as the preparation of metal oxide-Mg, where pure aluminum sheets $(10 \text{ cm} \times 10 \text{ cm} \times 1\text{mm})$ were utilized.

2. Characterization

The crystal structures were identified by X-ray diffraction (D max-2500, Rigaku, Tokyo, Japan) with Cu K α irradiation. UV-VIS-NIR spectroscopy (UV-3600, shimadzu, Kyoto, Japan) with BaSO₄ as reference was used to obtain the absorbance spectra of studied metal oxides. X-ray photoelectron spectra (XPS) were collected by X-ray photoelectron spectrometry (Escalab 250Xi, Thermos Fisher Scientific MA, USA) with monochromatic Al K α (150 W). The morphologies of the metal oxides were viewed by scanning electron microscopy (SEM, MERLIN VP compact, Zeiss). EPR spectra were recorded on a paramagnetic resonance spectroscope (EPR, FA-200, JEOL) at 300 K. The solid-state NMR measurements were carried out using a nuclear magnetic resonance spectrometer (JNM-ECZ 600R) with probe diameter of 3.2 mm. The impedance spectra were collected using an electrochemical workstation (PGSTAT204, Autolab) connected to a three-electrode cell containing 0.5 mol H₂SO₄ as electrolyte. The working electrodes were prepared by dispensing TiO₂ nanoparticles in mixed deionized water and ethanol (Volume ratio = 1:1) in presence of Nafion 117 (Aldrich) as binder. The mixed solution was then dipped on carbon fibre paper (Toray) with TiO₂ loading of 0.1 mg cm⁻². Ag/AgCl and carbon rod were used as reference and counter electrodes, respectively.

3. Photocatalytic property measurement

Rhodamine B (2.5×10^{-5} mol L⁻¹) and TiO₂ nanoparticles (1mg ml⁻¹) were mixed in 30 ml deionized water. The mixed solution was then ultrasonicated for 30 min followed by magnetic stirring for 1 h in the dark. The photocatalytic properties were measured using simulated solar light (micro solar 300, perfect light, Beijing, China) at light density of 100 mW cm⁻². The change in concentration of Rhodamine B was tested by UV-Vis spectrophotometry (UV-2600, shimadzu).

For hydrogen production experiments, 20 mg pristine or reduced TiO_2 nanoparticles was mixed with 100 ml methanol-water solution. The volume of methanol was 20 ml and employed as sacrificial reagent. Next, 0.1 mol H₂PtCl₆·6H₂O was added to the solution and the container was irradiated by UV light for 1 h to deposit platinum nanoparticles on TiO_2 nanoparticles as cocatalyst. Finally, the container was sealed and irradiated by 300 mW Xe lamp under full solar light for 3 h at light density of 100 mW cm⁻². The same solution was continually irradiated for 4 times for hydrogen generation stability experiments. The hydrogen content was determined every 30 min by gas chromatography (GC-7920).

4. Theoretical calculations

The density functional theory (DFT) calculations were performed with CP2K/Quickstep package.¹ The Heyd, Scuseria and Erzernhof (HSE06) functional methods with fraction α = 25% of Hartree-Fock (HF) exchange were typically employed.² The norm-conserving Goedecker, Teter and Hutter (GTH) pseudo potentials were employed to describe the core electrons.³ The wave functions of valence electrons were expanded using Gaussian function with molecularly optimized double-zeta polarized basis sets (m-DZVP).⁴ A 320 Ry cut off energy was utilized for auxiliary basis set of plane waves. All atoms were relaxed when the maximum residual force was converged to 0.02 eV Å⁻¹.

The structural model of A-TiO₂/Mg heterostructure was built using three layers of each anatase-(101) and Mg-(001) comprising of 291 atoms with vacuum spacing of 10 Å to prevent interactions between adjacent surfaces. The reduced TiO₂ were created by removing oxygen atoms (A-TiO₂-V₀, A-TiO₂-V₀/Mg) or adding H atoms to subsurface (A-TiO₂-2H, A-TiO₂-2H/Mg) of A-TiO₂. The 1×3 supercell of A-TiO₂ was made by three layers of anatase-(101) and 108 atoms with vacuum spacing of 10 Å to prevent interactions between adjacent surfaces. The reduced TiO₂ with different concentrations of adsorbed H were created by adding one, two or three H atoms to subsurface of A-TiO₂. The formation energy of V₀ and hydrogenation energy were calculated using Eqs. (1) and (2):

$$E_{formation} = E_{perfect} - E_{VO} + \mu_0 \tag{1}$$

$$E_{hydrogenation} = E_{perfect} - E_{2H} - 2\mu_H \tag{2}$$

where $E_{perfect}$ is the total energy of unreduced TiO₂ (A-TiO₂ or A-TiO₂/Mg), E_{VO} and E_{2H} represent the total energy of corresponding reduced TiO₂, and both μ_O and μ_H are respectively the chemical potential of O and H atoms referring to gas states.

The oscillator strength f_{cv}^{μ} in direction e_{μ} was calculated according to Eq. (3):

$$f_{cv}^{\mu} = \frac{2}{m_e(E_c - E_v)} |\langle v | \vec{e_{\mu}} \cdot \vec{r} | c \rangle|^2$$
(3)

where $\langle v |$ is the Kohn–Sham orbital corresponding to occupied states at VBM or gap states, $|c\rangle$ corresponds to unoccupied MOs above E_F , and both E_c and E_v represent respectively the eigenvalues of $|c\rangle$ and $\langle v |$.²



Figure S1. Mg 1s XPS of pristine TiO_2 and TiO_2 -Mg. The Mg 1S XPS result shows no presence of magnesium in the TiO_2 -Mg sample.



Figure S2. The atomic structures of both heterostructure anatase $TiO_2(101) / Mg(001)$ and anatase $TiO_2(101)$. (a) A- TiO_2/Mg ; (b) A- TiO_2 ; (c) A- TiO_2-V_0/Mg ; (d) A- TiO_2-V_0 ; (e) A- TiO_2-2H/Mg ; (f) A- TiO_2-2H/Mg ; (g) and (g) are the partially hydrogenated ones. Blue, red, green, orange balls are Ti, O, H, Mg atoms. Black circles represent oxygen vacancies (V₀). E_{formation} represents the formation energy of V₀,

E_{hydrogenation} stands for the adsorption energy of H atoms.



Figure S3. The charge density difference of $A-TiO_2/Mg$. (a) The crystal structure of $A-TiO_2/Mg$, and the balck curve highlights the interface between $A-TiO_2$ and Mg; (b) the 3D plot of charge density difference with the isosurface level of 0.004 eV/Å³, yelleow and blue means the accumulating and losing electrons, respectively.



Figure S4. Tauc plot of pristine TiO_2 and TiO_2 -Mg. To analyze the band gap energies, the Tauc plots are gathered. The band gaps of pristine TiO_2 and TiO_2 -Mg were estimated to 3.30 eV and 3.10 eV, respectively. Hence, the band gap energy of TiO_2 -Mg was slightly narrowed by about 0.20 eV.



Figure S5. Optical photographs of metal oxides. (a) In_2O_3 , In_2O_3 -Mg; (b) SnO_2 , SnO_2 -Mg; (c) Nb_2O_5 , Nb_2O_5 -Mg. The optical photographs indicated the reduction process turned all tested metal oxides to dark color, suggesting stronger absorption in visible light band.



Figure S6. Characterization of Mg reduced In_2O_3 , SnO_2 and Nb_2O_5 . (a)-(c) XRD plot; (d)-(f) UV–VIS-NIR absorbance spectra; (g)-(i) Tauc plot of pristine In_2O_3 , In_2O_3 -Mg, pristine SnO_2 , SnO_2 -Mg, pristine Nb_2O_5 , and Nb_2O_5 -Mg. The XRD patterns of metal oxides are same after reduction. Metal oxides-Mg showed stronger absorption in the visible and near infrared regions. The sharp absorption peaks apparently red-shifted. The change in absorption capacity could be attributed to existence of defects in metal oxides. The reduced metal ions acting as intermediate electronic states resulted in narrowed band gap energies and improved both visible and near-infrared light absorption, similar to TiO_2 analyzed above. The tauc plots were used to analyze the band gap energy changes of investigated metal oxides. The band gap energies of In_2O_3 , SnO_2 and Nb_2O_5 were estimated to 2.73 eV, 3.64 eV and 3.21 eV, respectively. For metal oxides-Mg, the corresponding band gap energies were 2.09 eV, 3.41 eV and 3.00 eV, confirming the effectiveness of the proposed reduction method for narrowing band gap energy of metal oxides.



Figure S7. Characterization of Li reduced TiO₂, In₂O₃, SnO₂ and Nb₂O₅ prepared by lithium sheet. (a) XRD pattern; (b) UV-VIS- NIR absorbance spectra; (c) Tauc plot of pristine TiO₂ and TiO₂-Li; (d) XRD pattern; (e) UV-VIS- NIR absorbance spectra; (f) Tauc-plot of pristine In₂O₃ and reduced In₂O₃-Li; (g) XRD pattern; (h) UV-VIS- NIR absorbance spectra; (i) Tauc plot of pristine SnO_2 and SnO_2 -Li; (j) XRD patterns; (k) UV-VIS- NIR absorbance spectra; (l) Tauc plot of pristine Nb₂O₅ and reduced Nb₂O₅-Li.The phase structure of TiO₂ composed of anatase and rutile remains unchanged. The TiO_2 -Li sample shows an optical absorption boost in visible and infrared region. Tauc plot analysis shows that the band gap energy of TiO₂-Li is 2.85 eV, which decreases 0.45 eV compared with the original TiO₂. The phase structure of In_2O_3 -Li is cubic, the same as the pristine. In_2O_3 -Li shows an optical absorption boost. Band gap energy of In₂O₃-Li is 1.69 eV. The phase structure of SnO₂-Li is tetragonal, which is the same as the pristine. Reduced SnO₂-Li shows an optical absorption boost in visible and near infrared region. Band gap energy of reduced SnO₂-Li is 3.41 eV from tauc plot, which decreases 0.23 eV compared with the original. The phase structure of reduced Nb_2O_5 -Li is orthohombic, which remains the same as the pristine. Reduced Nb₂O₅-Li shows an optical absorption boost in visible and near infrared region. Band gap energy of reduced Nb₂O₅-Li is 2.89 eV, which decreases 0.32 eV compared with the pristine from tauc plot.



Figure S8. Characterization of reduced TiO₂, In₂O₃, SnO₂ and Nb₂O₅ using aluminum sheet. (a) XRD pattern; (b) UV-VIS- NIR absorbance spectra; (c) Tauc plot of pristine TiO₂ and TiO₂-Al; (d) XRD pattern; (e) UV-VIS- NIR absorbance spectra; (f) Tauc-plot of pristine In₂O₃ and reduced In₂O₃-Al; (g) XRD pattern; (h) UV-VIS- NIR absorbance spectra; (i) Tauc plot of pristine SnO₂ and SnO₂-Al; (j) XRD patterns; (k) UV-VIS- NIR absorbance spectra; (l) Tauc plot of pristine Nb₂O₅ and reduced Nb₂O₅-Al.The phase structure of TiO₂ composed of anatase and rutile remains unchanged. The TiO₂-Al is 3.15 eV from tauc plot, which decreases 0.15 eV compared with the original. The phase structure of In₂O₃-Al is cubic, which is the same as the pristine. In₂O₃-Al is 2.56 eV, which decreases 0.18 eV compared with the pristine from tauc plot. The phase structure of SnO₂-Al is tetragonal, which is the same as the pristine. Reduced SnO₂-Al is 3.57 eV from tauc plot, which decreases 0.07 eV compared with the original. The phase structure of SnO₂-Al is 3.57 eV from tauc plot. Band gap energy of reduced SnO₂-Al is 3.57 eV from tauc plot, which decreases 0.07 eV compared with the original. The phase structure of SnO₂-Al is 3.57 eV from tauc plot.

orthohombic, which remains the same as the pristine. Reduced Nb_2O_5 -Al shows an optical absorption boost in visible and near infrared region. Band gap energy of reduced Nb_2O_5 -Al is 3.08 eV.



Figure S9. SEM morphology of pristine TiO_2 and TiO_2 -Mg. (a) SEM of pristine TiO_2 ; (b) SEM of TiO_2 -Mg. The average nanoparticle size of pristine TiO_2 is 25 nm, which are the same as TiO_2 -Mg nanoparticles. There are no changes in particle size and morphology after the reduction process.



Figure S10. VB XPS of pristine TiO₂ and TiO₂-Mg.



Figure S11. Band energy diagrams of pristine TiO_2 and TiO_2 -Mg. The band positions obtained by combining UV-VIS-NIR absorbance spectra and VB XPS are displayed. The valence band maximum

(VBM) of pristine TiO₂ was recorded as 2.45 eV. For TiO₂-Mg, the absorption onset was located at 2.41 eV with maximum energy blue-shifts towards vacuum level at 1.99 eV, correlated to band tail. The calculated band gap energies of pristine TiO₂ and TiO₂-Mg were estimated to 3.30 eV and 3.10 eV, respectively. Hence, the conduction band minimum (CBM) of pristine TiO₂ occurred at -0.85 eV while that of TiO₂-Mg at -1.11 eV.⁵ TiO₂-Mg presented upward shift of VBM and narrowed bandgap energy, associated with presence of Ti³⁺ species in TiO₂-Mg during reduction. These defects provided dispersed Ti³⁺ 3d below CBM and O 2p⁶ above VBM,⁶ promising for improved light absorption and photocatalysis.



Figure S12. XPS spectra of pristine TiO_2 and TiO_2 -Mg from different sites in reduced TiO_2 cylinder. (a) Diagram of four sites located in different positions in TiO_2 cylinder; (b) Ti 2p XPS spectra; (c) O 1s XPS spectra of the four sites. In order to prove the homogeneity of the reduction process, we take four sites from the TiO_2 -Mg cylinder and measure XPS spectra of the four samples. It can been seen from the Ti 2p XPS spectra that all the peak energy of the reduced samples shift about 0.25 eV to the lower binding energy compared to the pristine TiO_2 . The O 1s XPS spectras of the fours samples show obvious peaks around 531.2 eV, the areas of the four peaks are similar, which indicates the same content of OH bond in different sites.⁷ These results confirm that the TiO_2 nanoparticles are reduced uniformly, and the reduction degree is consistent.



Figure S13. Electrochemical impedance spectroscopy (EIS) of pristine pristine TiO_2 and TiO_2 -Mg. Electrochemical impedance spectroscopy (EIS) is also performed to characterize charge carrier transportation. EIS displays that the impedance radius of the pristine TiO_2 is smaller than that of TiO_2 -Mg, which suggests the improvement of conductivity and charge carrier transportation. The result can be explained as the existence of Ti^{3+} species in TiO_2 -Mg results in the increase of conductivity.⁸



Figure S14. Metal ions and O 1s XPS spectra of pristine metal oxide nanoparticles and reduced metal oxide nanoparticles. (a) In 3d XPS of pristine In_2O_3 and reduced In_2O_3 ; (b) Sn 3d XPS of pristine SnO_2 and reduced SnO_2 ; (c) Nb 3d XPS of pristine Nb_2O_5 and reduced Nb_2O_5 ; (d) O 1s XPS of pristine In_2O_3 and reduced In_2O_3 ; (e) O1s XPS of pristine SnO_2 and reduced SnO_2 ; (f) O1s XPS of pristine Nb_2O_5 and reduced Nb_2O_5 ; (f) O1s XPS of pristine Nb_2O_5 and reduced Nb_2O_5 . The binding energies of the metal ions in metal oxides all decrease after the reduction process, illustrating that metal ions with reduced state are implanted in metal oxide nanoparticles like TiO_2 analyzed above.⁹⁻¹¹ The fitting peaks in green line are attributed to lattice oxygen in metal oxides, while in purple line are correlated to OH bond. It is clear that the peak areas of OH bonds in these three metal oxides all show significant increases

after reduction process, which can be considered as oxygen defects implanted in metal oxides.¹²⁻¹⁴



Figure S15. SEM morphology of pristine metal oxides and metal oxides-Mg. (a) (b) (e) Pristine In_2O_3 , SnO_2 and Nb_2O_5 ; (b) (d) (f) In_2O_3 -Mg, SnO_2 -Mg and Nb_2O_5 -Mg. The average nanoparticle sizes of pristine In_2O_3 , SnO_2 and Nb_2O_5 are 20nm, 60nm, and 100nm, which are the same as reduced nanoparticles. There are no changes in particle size and morphology after the reduction process.



Figure S16. Digital image to show the color change when Mg sheet is in contact with compressed TiO_2 slice at different times, TiO_2 slice is not infiltrated with HCl solution. It is obvious that no color change occurs within 20 s if HCl solution is not dropped on TiO_2 , while the HCl infiltrated TiO_2 shows

rapid blue color diffusion under the same experimental condition.



Figure S17. (a) Digital image of obtained TiO_2 using Mg sheet-compressed TiO_2 cylinder-Mg sheet structure without HCl solution under the pressure ; (b) Digital image of obtained TiO_2 using Mg sheet-compressed TiO_2 cylinder-Mg sheet, where the TiO_2 cylinder is infiltrated with HCl solution. From Fig. S15, we can see that no reaction occurs when pressing the TiO_2 cylinder and Mg sheet without HCl soluton. By contrast, adding HCl solution to infiltrate TiO_2 cylinder, the whole TiO_2 cylinder turns dark blue instantly.



Figure S18. (a) Digital image of TiO_2 film deposited on Mg sheet; (b) Digital image of the obtained materials using the reduction approach. Fig. S16a shows the photograph of TiO_2 film deposited on Mg sheet. By dropping HCl solution on TiO_2 film, covering another Mg sheet, and applying pressure, TiO_2 film turns dark blue, which get the similar material as using the compressed TiO_2 cylinder, as shown in Fig. S16b.

Movie S1. The process of defects generation in TiO_2 when Mg sheet contacts with compressed TiO_2 slice infiltrated with HCl solution.

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